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Electron Spin Resonance Study of the Reaction between Sodium and Poly-4-vinylbiphenyl*

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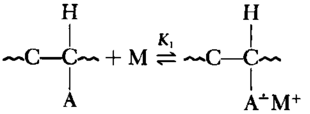
Summary

Poly-4-vinylbiphenyl (PVB) fractions of various molecular weights could be reacted with alkali metals in dimethoxyethane to form polyradical anions which were found to be stable at low temperature. The study of the line width of ESR signals obtained with high and low molecular weight PVB polyradical anions indicated electron delocalization over the polymer chains and extensive intramolecular exchange.

The extent of reaction of sodium with PVB was found to be smaller than with 4-ethylbiphenyl, the model unit segment. The theoretical interpretation of the hyperfine structure of the radical anion of 4-ethylbiphenyl helped to understand the ESR spectra of PVB polyradical anions degraded at room temperature.

It has recently been reported (*1,2*) that aromatic polymers are readily reduced by alkali metals at low temperatures to form polyradical anions. The same study established the existence of the following equilibrium:



$$\sim C-\underset{A}{\overset{H}{C}}\sim + M \overset{K_1}{\rightleftharpoons} \sim C-\underset{A^{\cdot-}M^{+}}{\overset{H}{C}}\sim \qquad (1)$$

where M and A denote an alkali metal and an aromatic moiety on a polymer chain, respectively. Equilibrium (1) is similar to equilib-

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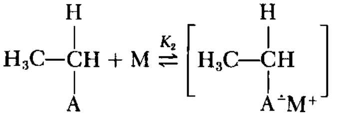
rium (2), which symbolizes the reaction between M and the ethyl derivative of the aromatic moiety. The latter represents a unit segment of the polymeric chain (3):



$$\mathrm{H_3C{-}\underset{\displaystyle A}{\overset{\displaystyle H}{CH}}} + \mathrm{M} \overset{K_2}{\rightleftharpoons} \left[\mathrm{H_3C{-}\underset{\displaystyle A^{\cdot-}M^{+}}{\overset{\displaystyle H}{CH}}}\right] \qquad (2)$$

It was also shown that if reaction (1) is carried out at room temperature or higher, it is accompanied by the formation of monomeric fragments, chain scission, and a decrease in free spin concentration with time as measured by the electron spin resonance (ESR) technique. These complications introduced by the occurrence of side reactions did not permit a detailed ESR study and a meaningful interpretation of the observed hyperfine structure. However, it is now found that at low temperatures (from −90°C to about 0°C) most or all of the side reactions can be eliminated. Therefore, the present ESR investigation was undertaken at low temperature to elucidate the origin and significance of the ESR results as well as to gain information concerning intramolecular electron transfer in polymers.

PURIFICATION OF REAGENTS AND EXPERIMENTAL TECHNIQUE

Tetrahydrofuran (THF), dimethoxyethane (DME), and 4-ethylbiphenyl (EB) were purified by a previously described procedure (*3*). Poly-4-vinylbiphenyl (PVB) of various molecular weights was synthesized by means of anionic polymerization of 4-vinylbiphenyl, using butyllithium as initiator. The isolated polymers were subsequently fractionated and their molecular weight distribution determined (*4*) (see Table 2). The preparation of dilute or concentrated solutions of polyradical anions and the transfer of reagents were accomplished by means of an established vacuum technique (*5*).

ESR measurements were made on the Varian V-4502 spectrometer equipped with 100 kHz field modulation and the Varian V-4532 dual sample cavity. Spin concentrations were measured at room temperature by a method previously reported (*6*) with the aid of a standard pitch sample. The V-4540 variable temperature accessory attached to the dual sample cavity afforded temperature control. At temperatures other than ambient, spin concentrations were measured by comparing graphical first moments with those obtained at room temperature. The absorbance of a pitch sample kept in the front half of the dual sample cavity allowed the detection of changes in cavity Q as the temperature of the other samples was varied. Microwave power was measured with a Hewlett Packard HP-431B power meter in conjunction with an HP-X486A thermistor mount attached to the 20-db directional coupler built into the Varian microwave bridge. The power transmitted to the dual sample cavity was 50 times the reading on the power meter. A reading of 0.03 mW, corresponding to a klystron output attenuation of about 10 db, permitted a maximum ESR absorption without saturation broadening of the individual hyperfine lines in the spectrum of EB.

RESULTS

Poly-4-vinylbiphenyl

The ESR signal of PVB on sodium at −78°C consisted of a single Lorentzian line whose width decreased continuously with time as the concentration of polyradical anions increased until the reaction had gone to completion. When the samples were kept at −90°C, no change of line width was observed on 50-fold dilution of 10^{-3} *M* and 10^{-5} *M* polyradical anions in either THF or DME. An independent check by liquid gas chromatography showed absence of monomeric fragments in PVB-DME solutions reacted with sodium at low temperature for 30 hr. In addition, the line width decreased with increasing polymer molecular weight (Table 1). Thus it appears that the line-width changes are due to exchange narrowing and motional narrowing of unpaired electrons delocalized along a polymer chain. This problem has been considered theoretically by McConnell (7).

TABLE 1

ERS Line Widths[a] (in Gauss) for EB and PVB in Dimethoxyethane (10^{-3} *M*)

	Reaction time on sodium		
Molecular weight	30 min	2 hr	30 hr
182 (EB)	Overall line width = 25.1 gauss		
10,500 (PVB)	11	1.7	1.3
69,000 (PVB)	4.5	3.4	1.2
437,000 (PVB)	2.0	1.6	1.0

[a] Line widths listed are distances between first-derivative peaks.

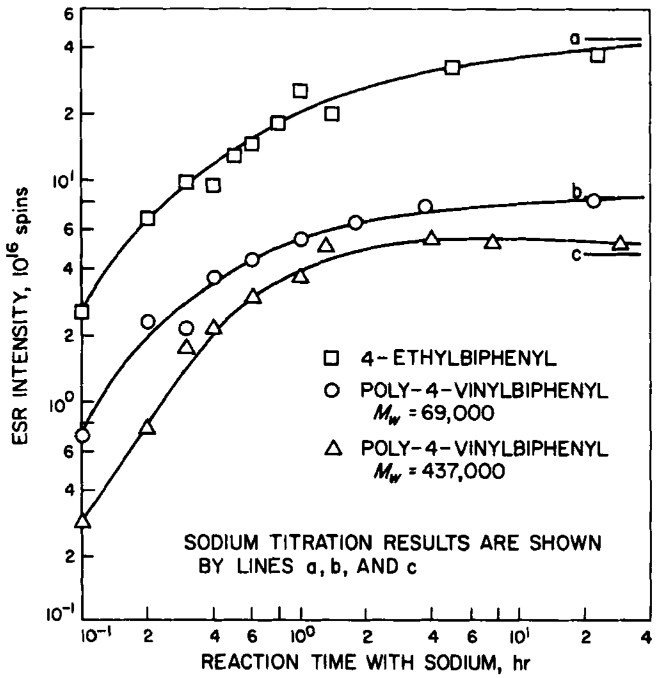


FIG. 1. Rate of formation and sodium titration analysis of radical anions of EB and PVB.

TABLE 2

ESR and Sodium Titration Results

	M_w	M_w/M_n^a	Concentration of Na, moles/liter[b]	ESR intensity[c]		$\frac{K^f_{\text{polymer}}}{K_{\text{monomer}}}$
				Calcd.[d]	Measured[e]	
EB	182	1	0.0076	46	42	—
PVB	10,500	<1.5				
PVB	69,000	1.27	0.0014	8.4	8.6	0.18
PVB	437,000	1.36	0.00078	4.7	5.3	0.10

[a] M_w, weight-average molecular weight determined by light scattering; M_n, number-average molecular weight from osmometry data.

[b] Titration (with 0.01 *N* HCl) results after 30 hr reaction time.

[c] Per 0.1 cc in units of 10^{16} unpaired electron spins.

[d] From Na titration results.

[e] By comparison with a pitch-in-KCl standard.

[f] *K* denotes constant for equilibrium (1).

Figure 1 and Table 2 demonstrate that the equilibrium constant of Eq. (1) decreases as the polymer molecular weight increases, presumably because of repulsion among unpaired electrons on the same polymer chain. In addition, sodium titration performed after approximately 30 hr of reaction time (see Fig. 1) confirms the lower value of the equilibrium constant for PVB than for EB and the fact that the ESR signal intensity of a sample is proportional to its sodium content.

Figure 2 shows the decrease of unpaired spin concentration with increase of temperature for EB and PVB of different molecular weights. The product of unpaired spin concentration and temperature was plotted rather than spin concentration alone to correct for Curie law paramagnetism. The changes in spin concentration are

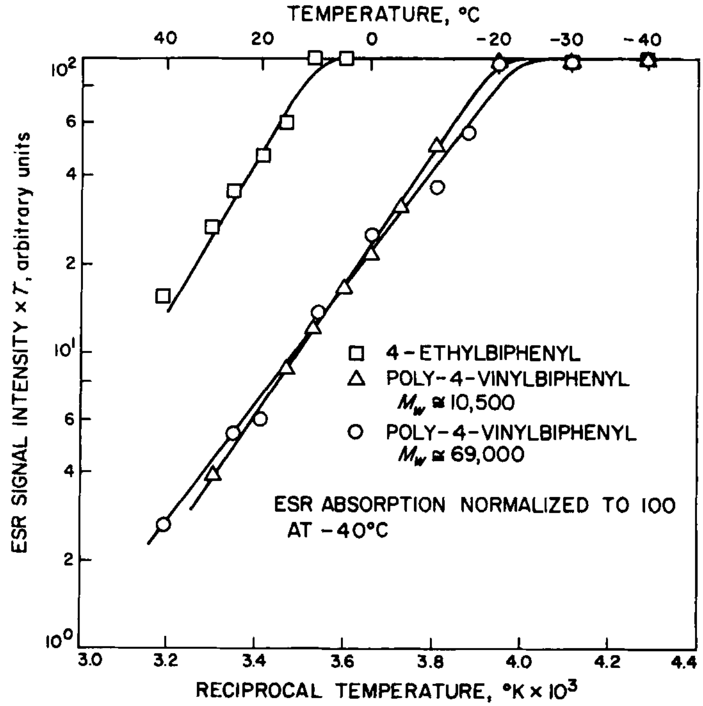


FIG. 2. Temperature dependence of ESR absorption for EB (10^{-3} *M*) and two PVB polymers (10^{-3} *M*) reacted with sodium for 30 hr at −80°C in DME. A different ordinate scale was used for each curve as only the slope in its linear region is of interest. The ESR absorption of each curve is normalized to 100 at −40°C.

understood on the basis of the equilibria (1) and (2). Sodium precipitation from solution was observed as the temperature was increased, in agreement with previous observations (3).

4-Ethylbiphenyl

Polyradical anions were found to degrade (*2,3*) when heated or allowed to stand several hours at room temperature, forming diamagnetic carbanions with concomitant decrease in ESR absorption. In the present studies the overall ESR absorption decrease for PVB is confirmed but, in addition, the appearance of the EB radical anion spectrum superimposed upon that of the polymer is observed (Fig. 3). Figure 3a is the ESR absorption of a mixture of PVB and 2% by weight of EB. Figures 3b and 3c represent spectra of PVB after standing overnight at room temperature. The width of the hyperfine lines appears to be different in each of the three spectra, and this results in differences in the relative intensities. However, it is apparent that the positions of all discernable lines are identical when the spectra are obtained at higher gain. By comparing the relative intensities of the spectra of EB and PVB in Figs. 3a, 3b, and 3c, one may conclude that sample 3b and 3c contain approximately 2% EB. Wehave been able to detect as little as 0.2% by weight EB in a mixture of EB and PVB by examining high-gain spectra similar to that of Fig. 3a.

The hyperfine structure of PVB (after reaction on Na in either THF or DME) was assumed to be due to the superposition of the EB radical anion spectrum over the single line signal of the polymer. To prove this unequivocally it was found necessary to obtain a well-resolved ESR spectrum of EB radical anion and to reproduce its structure theoretically.

Figure 4 shows the experimentally obtained (a), and the theoretically reconstructed (b) ESR spectrum of the EB radical anion (5×10^{-4} *M*) in DME at −80°C (identical spectra are obtained with either K or Na as the alkali metal counterion). Better spectral resolutions could be achieved in DME than in THF in agreement with previous findings (*8*). In addition, alkali metal hyperfine splittings in the more polar DME appear to be smaller or nonexistent (*9,10*). The best resolution was realized at −80°C. At lower temperatures increased viscosity of the solvent results in anisotropic broadening of the individual hyperfine lines, and at higher temperatures exchange broadening was observed.

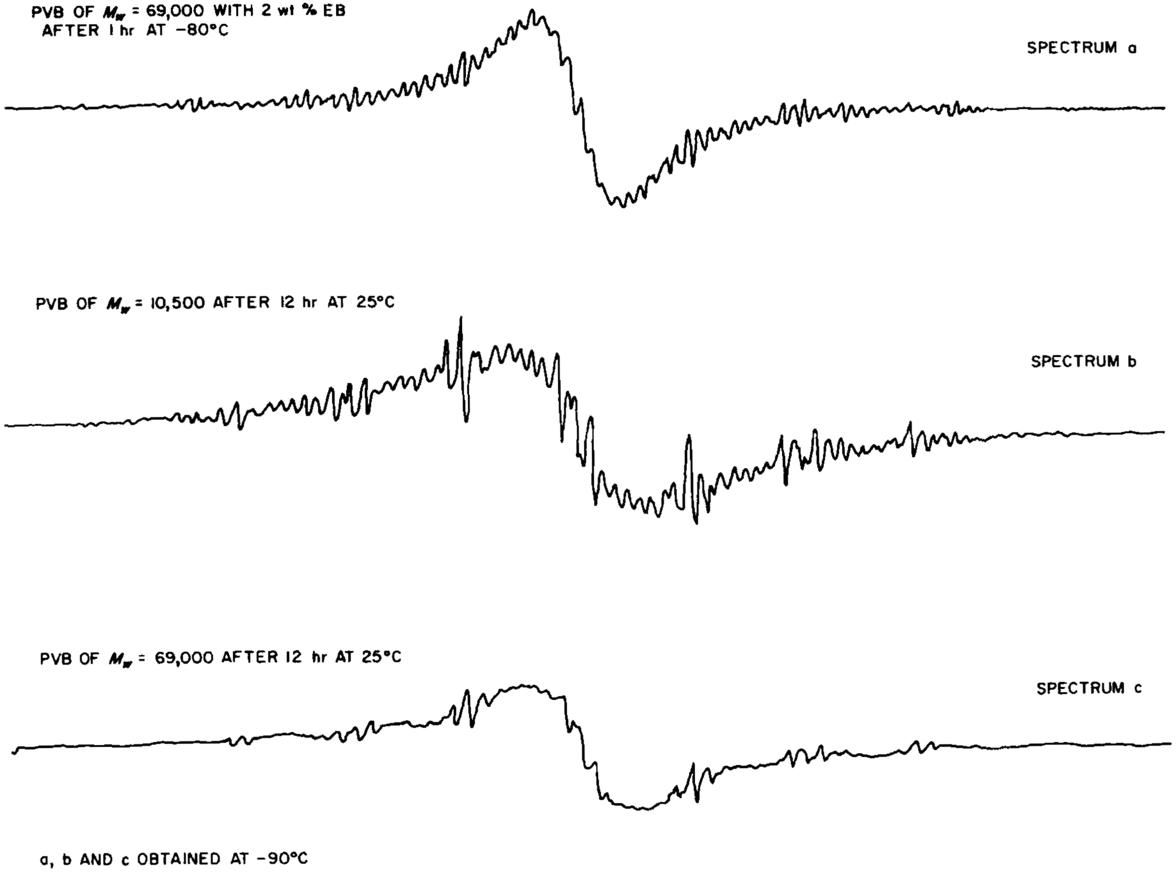


FIG. 3. ESR absorption of a mixture of EB and PVB on sodium. (a) PVB of $M_w = 69{,}000$, containing 2% EB by weight, after 1 hr at −78°C; (b) PVB of $M_w = 10{,}500$ after 12 hr at 25°C; (c) PVB of $M_w = 69{,}000$ after 12 hr at 25°C. All three spectra were obtained at −90°C.

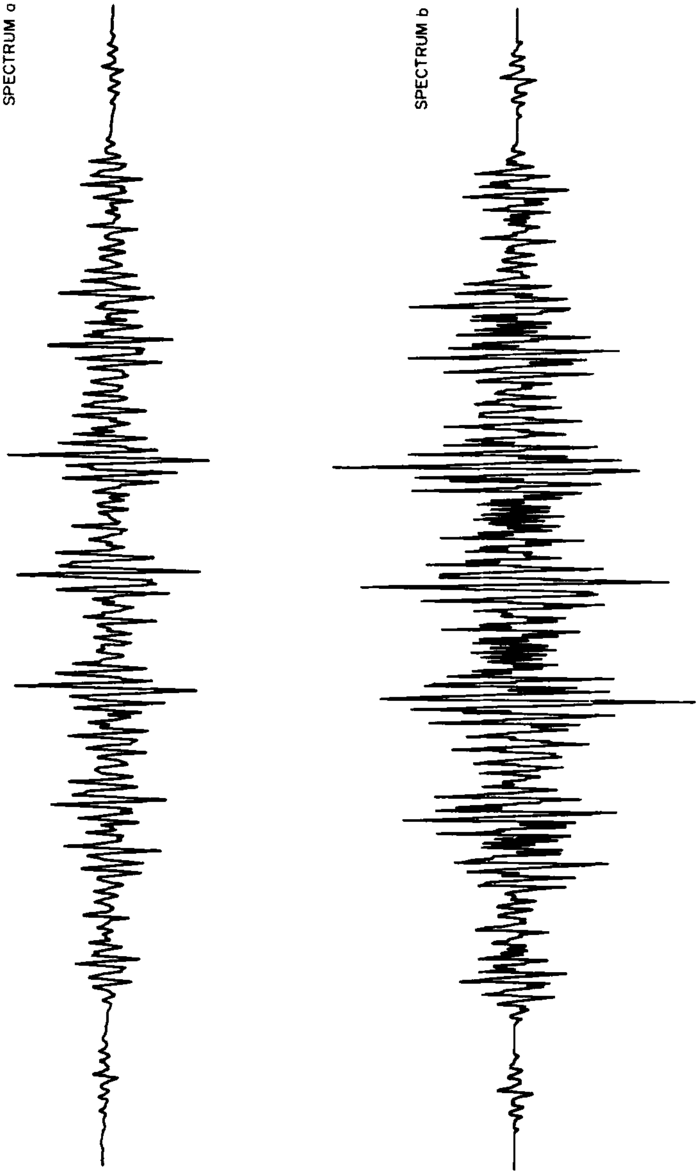
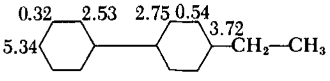


FIG. 4. Experimental (a) and theoretical (b) ESR spectrum of EB radical anion (5×10^{-4} *M*) in DME at −80°C.

Figure 4b was obtained with a Japan Electron Optics Laboratory Model JRA-1 spectrum accumulator. The programmed hyperfine splitting constants are as follows: one hydrogen nucleus of 5.34 gauss, and five groups of two equivalent hydrogen nuclei of 3.72, 2.75, 2.53, 0.54, and 0.32 gauss. A line width of 0.12 gauss was used for each of the 486 theoretical lines.

There are small differences between spectra 4a and 4b; however, a splitting constant variation of as little as 0.01 gauss results in a marked change in the nature of the computed spectrum, especially in the regions between the more intense groups of lines. It is estimated that the quoted splitting constants are correct within ±0.02 gauss.

The assignment of splitting constants is usually based on a correlation between odd-electron spin densities obtained by a Hückel molecular orbital calculation. The presence of an alkyl substituent on the diphenyl ring make the results of such a calculation rather uncertain. According to the work of Ishizu (8) with 4-methylbiphenyl, the following assignment seems plausible:



The analysis of the hyperfine structure of the EB radical anion reveals that the highest unpaired density is in the para position, but a precise assignment of the remaining splitting constants must await a careful ESR study of other substituted biphenyls.

CONCLUSIONS

The significance of the above results may be summarized as follows: On the basis of single line-width changes (Table 1) in ESR spectra of PVB with increasing concentration of reacted alkali metal, there is little doubt that (a) electron transfer takes place from sodium to aromatic side chains of the polymer. Chemical analysis indicates that about 20% of the aromatic moieties may thus be complexed resulting in an unpaired electron on every fifth aromatic ring, on the average; (b) intramolecular electron exchange or electron delocalization along a polymer chain does occur. This conclusion is substantiated by the fact that no change of line width was observed on maximum dilution of specimens exhibiting exchange narrowed lines. Furthermore, calculations based on results of Fig. 1 show that the longer the chain, the larger the number of unpaired electrons per chain. Thus the probability of intramolecular exchange increases with molecular weight in agreement with experimental results (Table 1).

A comparison of equilibrium (1) with equilibrium (2) brings out an important problem in polymer chemistry: the reactivity of the same group on a low molecular weight analogue. The classic investigations carried out by Flory established the principle of equal reactivity for a broad range of polymeric reactions (*11,12*). In spite of the fact that this principle has been found to hold true for many systems, numerous examples may be quoted where functional groups attached to a high polymer have reactivities deviating to a significant extent from those of monofunctional analogues (*13*).

The most understandable deviations were observed in cases where an electrostatic charge placed on a polymer chain was exercising a profound effect over a considerable distance. The best test of this effect is the ionization equilibrium of simple polyelectrolytes. For instance, the ionization constant of polyacrylic acid has been shown to vary greatly with the fraction of ionized carboxyl groups (*14*). Thus a given group is harder to ionize if a neighboring group is ionized.

In our case, we will assume that a partial negative charge is introduced by electron transfer from an alkali metal to aromatic molecules linked to the polymeric chain. It would, therefore, become progressively more difficult to introduce new negative charges after a certain number of electrons have been transferred, and it is not surprising to find that K polymer < K monomer (Table 2), the former representing the equilibrium constant for reaction (1), and the latter the equilibrium constant for reaction (2). Our preliminary rate studies (Fig. 1) seem to confirm the decrease of reactivity with reaction time. However, detailed kinetic studies are necessary to throw more light on this system.

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Zusammenfassung

Poly-4-vinylbiphenyl (PVB) Fraktionen verschiedenen Molekulargewichts konnten in Dimethoxyäthan mit Alkalimetallen zu Polyradikalanionen reagiert werden. Letztere waren bei tiefer Temperatur stabil. Die Untersuchung der Linienbreite des ESR Signals von hoch-und niedermolekularen PVB Polyradikalanionen ergab eine Elektronendelokalisation über die ganze polymere Kette und intensiven intramolekularen Austausch.

Das Ausmass der Reaktion von Natrium mit PVB war geringer als mit 4-Äthylbiphenyl, der monomeren Modellsubstanz. Die theoretische Interpretation der Hyperfeinstruktur des Radikalanions des 4-Äthylbiphenyls unterstützte die Auswertung der ESR Spektren von bei Zimmertemperatur abgebauten PVB Polyradikalanionen.

Résumé

Les fractions de poly-4-vinylbiphenyl (PVB) à masses moléculaires variées réagissent avec les métaux alcalins dans le diméthoxyéthane avec formations d'anions polyradicalaires, stables à des températures basses. L'étude de la largeur de la raie des signaux ESR obtenus avec des anions polyradicalaires de PVB à masses moléculaires elevées ou basses, indique l'occurence d'une delocalisation d'electrons le long de la chaine et d'un échange intramoléculaire considérable.

On a trouvé que la reaction du sodium avec PVB n'est pas si étendue qu'avec l'éthyl-4-biphényl, le modèle d'un seul segment. L'interprétation théorique de la structure hyperfine de l'anion radical de l'éthyl-4-biphenyl facilite la compréhension des spectra ESR des anions polyradicalaires de PVB degradé à température ambiante.

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